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(54) CURABLE COATING COMPOSITIONS COMPRISING VINYLURETHANES

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:-

The present invention relates to a curable coating composition which comprises a vinylurethane.

Coating compositions comprising solutions of high molecular weight or low molecular weight unsaturated compounds in vinyl monomers have been disclosed. If vinyl compounds which copolymerize rapidly, e.g. acrylic compounds, are used, such systems can be cured with high energy radiation. However, acrylic compounds have the disadvantage that they are usually toxic and cause severe irritation of the skin.

A process has been disclosed in German Laid-Open Application DOS 2,064,701 for the manufacture of coatings by curing olefinically unsaturated polymeric materials containing urethane groups, these materials, with or without admixture of other olefinically unsaturated monomeric compounds, being cured by means of ionizing rays; the olefinically unsaturated polymeric material containing urethane groups comprises at least two

$$CH_2=CH\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}$$

units and has been obtained by reacting hydrolic oligomers or polymers of molecular weight from 500 to 10,000 with vinyl isocyanate. However, these products are rather unsuitable for certain applications, where a particularly high degree of crosslinking is required. In some cases, a very low viscosity of the component which forms the binder is desirable, to facilitate its use.

The present invention therefore seeks to provide improved coating compositions particularly those which, in spite of being processed at a low viscosity, cure very actively.

We have found that good results can be achieved by using special mixtures of certain vinyl urethanes and other unsaturated compounds.

The present invention provides a curable coating composition which comprises a mixture of A) one or more olefinically unsaturated compounds having a molecular weight of from 70 to 20,000 and a boiling point at standard pressure of above 50°C and
B) one or more vinylurethanes copolymerizable with A) but differing therefrom, in which component (B) is a reaction product of vinyl isocyanate and a polyol having a molecular weight of less than 500 and the weight ratio of the components A:B is from 99:1 to 30:70.

The following details relating to the components on which the coating compositions of the invention are based should be noted.

(A) The olefinically unsaturated compounds (A) should have a boiling point at standard pressure of above 50°C, preferably above 100°C. Lower-boiling compounds are, in general, less suitable, since they evaporate too easily after applying the coating compositions and before curing them. This can alter the analysis of the coating composition and can also lead to pollution of the environment by malodorous and, in some cases, toxic monomers. Compounds having a vapor pressure of less than 10 mm Hg at 100°C are therefore particularly preferred for finishes and printing inks which do not pollute the environment.

The molecular weight of component A can vary within wide limits, from 70 to 20,000, i.e. either low molecular weight or high molecular weight compounds may be employed. The compounds may be mono-olefinically unsaturated or have a higher degree of unsaturation.

Examples of suitable components A are:

1. Esters of unsaturated monocarboxylic acids or dicarboxylic acids, for example esters of acrylic acid, methacrylic acid, α-cyanoacrylic acid, crotonic acid, cinnamic acid, sorbic acid, maleic acid, fumaric acid or itaconic acid, with aliphatic, cycloaliphatic or aromatic-aliphatic monohydric to tetrahydric alcohols of 3 to 20 carbon atoms, e.g. methyl acrylate and methacrylate, n-, i- and t-butyl acrylate and methacrylate, 2-ethylhexyl acrylate, lauryl acrylate, dihydrodicyclopentadienyl acrylate and methacrylate, methylglycol acrylate, hydroxyethyl acrylate and methacrylate, hydroxypropyl acrylate and methacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, neopentyl-glycol diacrylate and dimethacrylate, 1,4-dimethylolcyclohexane diacrylate, pentaerythritol triacrylate, tetraacrylate, trimethacrylate and tetramethacrylate, ethyl α-cyanoacrylate, ethyl crotonate, ethyl sorbate, diethylmaleate, diethyl fumarate and the diacrylate and dimethacryate of oxyalkylated bisphenol A.

2. Amides of acrylic acid or methacrylic acid which may or may not be substituted by alkyl, alkoxyalkyl or hydroxyalkyl at the nitrogen, e.g. N,N'-dimethylacrylamide, N-isobutylacrylamide, diacetoneacrylamide, N-methylolacrylamide, N-methoxymethylacrylamide, N-butoxymethylacrylamide, N-butoxymethylmethacrylamide and ethylene glycol bis-(N-methylolacrylamide) ether.

3. Vinyl esters of monocarboxylic acids or dicarboxylic acids of 2 to 20 carbon atoms, e.g. vinyl acetate, vinyl propionate, vinyl 2-ethylhexanoate, vinyl versatate ("Versatic" is a Registered Trade Mark) or divinyl adipate.

4. Vinyl ethers of monohydric or dihydric alcohols of 3 to 20 carbon atoms, e.g. isobutyl vinyl ether, hexyl vinyl ether, octadecyl vinyl ether, ethylene glycol divinyl ether, diethylene glycol divinyl ether, butanediol divinyl ether and hexanediol divinyl ether.

5. Mono-N-vinyl compounds, e.g. N-vinylpyrrolidone, N-vinylpiperidone, N-vinylcaprolactam, N-vinylmorpholine, N-vinyloxazolidone, N-vinylsuccinimide, N-methyl-N-vinylformamide, N-vinylcarbazole and divinylureas, e.g. N,N'∂ divinylethyleneurea and divinylpropyleneurea.

6. Styrene and its derivatives, e.g. α-methylstyrene, 4-chlorostyrene and 1,4-divinylbenzene.

7. Allyl ethers and allyl esters, e.g. trimethylolpropane diallyl ether, trimethylolpropane triallyl ether, pentaerythritol triallyl ether, diallyl maleate, diallyl fumarate and diallyl phthalate.

8. Unsaturated polyesters having a molecular weight of from 500 to 5,000 and containing from 0.5 to 10 double bonds per 1,000 molecular weight units, the polyesters being manufactured from, for example,

a) from 10 to 70 per cent by weight of one or more α,ß-unsaturated dicarboxylic acids, e.g. malcic acid, fumaric acid or itaconic acid,

b) from 0 to 60 per cent by weight of one or more saturated aliphatic, optionally chlorine-substituted cycloaliphatic or aromatic dicarboxylic acids, e.g. succinic acid, adipic acid, tetrahydrophthalic acid, hexahydrophthalic acid, hexachloroendomethylenetetrahydrophthalic acid, cyclohexane-1, 4-dicarboxylic acid, phthalic acid, isophthalic acid or terephthalic acid,

c) from 20 to 80 per cent by weight of one or more aliphatic, cycloaliphatic or non-phenolic aromatic diols, e.g. ethylene glycol, diethylene glycol, triethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, butane-1,3-diol, butane-1,4-diol, but-2-ene-1,4-diol, neopentyl-glycol, hexane-1,6-diol or oxyalkylated bisphenol A,

d) from 0 to 5 per cent by weight of one or more tricarboxylic acids or tetracarboxylic acids, e.g. trimellitic acid, pyromellitic acid or benzenetetracarboxylic acid,

e) from 0 to 10 per cent by weight of one or more monocarboxylic acids, e.g. acetic acid, propionic acid or benzoic acid,

f) from 0 to 5 per cent by weight of one or more trifunctional or tetrafunctional alcohols, e.g. glycerol, trimethylolpropane or pentaerythritol, and

g) from 0 to 10 per cent by weight of one or more monofunctional alcohols, e.g. methanol, ethanol, propanol or butanol.

9. Unsaturated epoxy resins which have been manufactured from, for example,

a) a monofunctional epoxide and acrylic acid or methacrylic acid, as described in U.S. Patent 2,484,487,

b) a bifunctional epoxide and an unsaturated fatty acid, as described in U.S. Patent 2,456,408,

c) a polyfunctional aromatic epoxide and crotonic acid, as described in U.S. Patent 2,575,440, or

d) a polyfunctional aromatic or aliphatic glycidyl ether and acrylic acid or methacrylic acid, as described in U.S. Patent 2,824,851.

10. Unsaturated polyurethanes obtained from hydroxyalkyl acrylates and diisocyanates,

with or without polyols or polyamines, for example saturated or unsaturated polyester-polyols, polyether-polyols or copolymer-polyols, as are described, for example, in German Laid-Open Application DOS 1,644,797 or, for printing ink purposes, in German Laid-Open Application DOS 2,358,948.

11. Unsaturated copolymers, for example manufactured by reacting.
a) copolymers, containing maleic anhydride groups, with unsaturated alcohols, for example as described in German Laid-Open Application DOS 2,050,893 or
b) acrylic ester copolymers or polyesters, containing carboxylic acid groups, with olefinically unsaturated epoxides, e.g. glycidyl acrylate.

12. Butadiene polymers in which the double bonds are predominantly present as vinyl side groups.

13. Diallyl phthalate prepolymers.

Of course, mixtures of the various unsaturated compounds A may also be used.

The compounds listed under 1, 2, 8, 9, 10 and 11 above, and their mixtures, are particularly preferred components A.

(B) The vinylurethanes which may be used as component (B) are reaction products of vinyl isocyanate and one or more polyols having molecular weights of less than 500, preferably less than 400. Examples of suitable polyols are linear or branched aliphatic, cycloaliphatic and araliphatic diols, e.g. ethylene glycol, 1,2- and 1,3-propylene glycol, butanediol, pentanediol, hexanediol, 3-methyl-pentane-1,5-diol, neopentyl-glycol, 2-methyl-2-propyl-propane-1,3-diol, decanediol, cyclohexanediol, cyclohexanedimethanol, tricyclodecanedimethanol and bis-hydroxymethylbenzene; diols containing ether groups, e.g. diethylene glycol, triethylene glycol, dipropylene glycol, other oligomers of ethylene oxide and propylene oxide, and adducts of ethylene oxide or propylene oxide with diols or dihydric phenols; triols, e.g. glycerol, trimethylolpropane, butane-1,2,4-triol, pentane-1,2,5-triol, hexane-1,2,6-triol, tris-hydroxyethyl isocyanurate, and oxyethylation or oxypropylation products of trihydric alcohols or phenols; alcohols of higher functionality, e.g. pentaerythritol, dipentaerythritol, sorbitol, mannitol and oxyethylation and oxypropylation products of the said polyhydric alcohols or of diamines; and ester-diols, e.g. the hydroxypivalic acid ester of neopentyl-glycol, and condensation products of dicarboxylic acids with excess diol, which may or may not contain co-condensed higher-functional carboxylic acids or alcohols.

To manufacture the vinylurethanes the polyol(s) are reacted with vinyl isocyanate, in general in such an amount as to provide from 0.7 to 1.2, preferably from 0.9 to 1.05, moles of vinyl isocyanate per equivalent of polyol, i.e. per mole of OH groups.

Mixtures of reaction products of vinyl isocyanate with several of the above polyols may be used as component (B).

The properties of the products can, to a certain degree, be suited to special requirements by appropriate variation of the starting components.

Components A and B are employed in the weight ratio of from 99:1 to 30:70, preferably from 95:5 to 50:50.

In general, components (A) and (B) are mixed at from 20 to 80°C in conventional mixing equipment, or using conventional stirring equipment.

The coating composition of the invention may, depending on its intended use, also contain relevant additives, for example:

1. From 0 to 70, preferably from 10 to 50, per cent by weight of inorganic or organic pigment, e.g. carbon black, titanium dioxide, chalk, baryte, zinc white, lithopone, chromium yellow, yellow iron oxide or complex pigments, e.g. phthalocyanines, azo pigments, anthraquinone colorants and quinacridone pigments.
2. From 0 to 10, preferably from 0.001 to 3, per cent by weight of dye, e.g. eosin, crystal violet or malachite green.
3. From 0 to 10, preferably from 1 to 5, per cent by weight of leveling agent, e.g. butyl acetate, butanol, silicones or thinners.
4. From 0 to 1, preferably from 0.001 to 0.5, per cent by weight of inhibitor.
5. From 0 to 70, preferably from 10 to 50, per cent by weight of filler.
6. From 0 to 10, preferably from 1 to 5, per cent by weight of diluent.
7. From 0 to 70, preferably from 10 to 50, per cent by weight of inert synthetic resin, e.g. aminoplasts and alkyd resins.
8. From 0 to 7, preferably from 0.5 to 5, per cent by weight of wax.
9. From 0 to 5, preferably from 0.2 to 5, per cent by weight of thixotropic agent.

The coating compositions are cured by copolymerization of components A and B. This may be effected thermally, by direct heating, by means of infrared radiation or with the aid of an initiator, but preferably by using high energy radiation.

For the thermal polymerization, temperatures of from 20 to 200°C are generally employed; conventional initiators, e.g. organic peroxides or azo compounds, and accelerators,

e.g. cobalt salts, may be added in amounts of from 0.5 to 6 per cent by weight.

Radiation curing may be effected with UV rays or by electron beams. In the former case, a conventional photoinitiator, such as are described, for example, by B.J. Kosar in "Light Sensitive Systems", Wiley, 1965, pages 158-193, may be added. Preferably, the following are used: Benzoin, benzoin ethers, diacetyl, benzil, benzil monoketals, benzophenone, Michler's ketone, xanthones, anthraquinones, sulfur compounds, e.g. disulfides, thiols and dithiocarbamates, and carbonyl compounds, e.g. triphenylphosphine-iron tetracarbonyl in conjunction with chlorine donors, each in amounts of from 1 to 3 per cent by weight. Details of the method of curing by UV radiation are to be found in "Photopolymerization" by H. Barzynski, K. Penzien and O. Volkert in Chemiker-Zeitung *96* (1972), 545-551, and in German Laid-Open Application DOS 2,251,933. Electron beam curing is described in detail in German Laid-Open Application DOS 2,049,715 cited above, in which further details regarding advantageous coating thicknesses, radiation doses and irradiation times may also be found.

The coating compositions may be used for the production of coatings and finishes on metals, wood, plastic, leather and paper. These coatings may be used as protective layers or for decorative purposes.

The coating compositions may also be used as a photopolymer layer for print carriers, e.g. relief print plates or planographic print plates, or for photoresists. In such cases, they are cured by image-wise irradiation of the coated carrier; no curing occurs in the unexposed zones and these parts of the layer are dissolved out again.

Finally, the coating compositions may also be used for the manufacture ofUV-curing printing inks and print pastes. Using such inks and pastes, substrates, e.g. paper, metals or plastic films, are printed with the pigment-containing binders in order to apply a layer from about 0.5 to 5 μm thick. The binders cure very rapidly on ultraviolet irradiation and the ink becomes fixed to the substrate. The printing inks manufactured using the coating compositions of the invention are distinguished by extremely rapid drying even if only 1 or 2 ultraviolet lamps are used in the case of four-color printing, and by very high printong speeds. The drying prints have very good scuff resistance. This would seem to be more in line with what is needed in multi-color printing. This resistance is much improved over conventional ultraviolet printing inks in the case of colors which are, from this point of view, particularly critical in ultraviolet printing, e.g. blue and black. These remarks apply particularly to prints produced at maximum print speeds and hence with minimum irradiation times.

If no pigments are added, the binders may be used as overprinting varnishes or as clear coatings.

In the Examples, parts and percentages are by weight.

EXAMPLE 1

0.07 part of dibutyl-tin dilaurate is added to a solution of 134 parts of trimethylolpropane in 300 parts of ethyl acetate and 207 parts of vinyl isocyanate are added dropwise in the course of 40 minutes at from 50 to 60°C, whilst stirring. The reaction is then allowed to continue for from 1 to 2 hours, until the isocyanate content has fallen to below 0.1%. The mixture is then cooled to about 10°C, whereupon the reaction product substantially cystallizes out, and the crystals are filtered off. After recrystallization from ethyl acetate and drying under reduced pressure at room temperature, 320 parts of trimethylolpropane-trivinylurethane are obtained. A mixture of 50 parts of this material and 50 parts of trimethylolpropane triacrylate is applied at a thickness of 60 μm to a surface-filled wooden board and is cured with 320 KV electrons at a belt speed of 100 m/min, corresponding to a dose of 0.7 Mrad. A tack-free scratch-resistant coating of great hardness (König pendulum hardness: 190 seconds) and high gloss is obtained.

EXAMPLE 2

If the procedure of Example 1 is followed, but instead of 134 parts of trimethylolpropane 204 parts of the neopentylglycol ester of hydroxypivalic acid are used, and instead of 207 parts only 138 parts of vinyl isocyanate are used to manufacture component (B), a viscous mass, which solidifes after from 1 to 2 days, is obtained after removing the solvent. A mixture of 20 parts of this reaction product with 40 parts of butane-1,4-diol diacrylate and 40 parts of unsaturated polyester obtained from 2 moles of maleic anhydride, 1 mole of hexachloroendomethylenetetrahydrophthalic acid, 2 moles of neopentyl-glycol and 1 mole of propylene glycol (acid number : 30 mg of KOH/g) is applied, as described in Example 1, as a layer 80 μm thick to a surface-filled wooden board, and cured with 320 KV electrons at a belt speed of 60 m/min, corresponding to a dose of 1.17 Mrad. A very hard, scratch-resistant coating (König pendulum hardness: 205 seconds) is obtained.

EXAMPLE 3

A mixture of 10 parts of trimethylolpropane-trivinylurethane, 40 parts of butane-1,4-dioldiacrylate and 50 parts of a reaction product of one mole of a diglycidyl ether, based on bisphenol A (epoxide equivalent weight: 340) with 2 moles of acrylic acid is applied, as described in Example 1, as a layer 70 μm thick to a surface-filled hard fiberboard and cured under the conditions described in Example 2. The cured, tack-free coating has a König pendulum hardness of 200 seconds.

Our copending GB patent application No. 33899/77 (Serial No. 1583413) discloses and claims curable binders for coating compositions comprising

(i) one or more olefinically unsaturated compounds containing urethane groups, which are a reaction product of vinyl isocyanate and a compound which contains at least one hydroxyl group and at least one radical of an ester of an α,β-olefinically unsaturated carboxylic acid of 3 to 6 carbon atoms, and optionally also comprising

(ii) one or more further olefinically unsaturated compounds which are copolymerizable with but different from the olefinically unsaturated compounds which are copolymerizable with but different from the olefinically unsaturated compound(s) containing urethane groups.

We make no claim herein to coating compositions comprising components (i) and (ii) above in a weight ratio of (i): (ii) of from 70:30 to 1:99.

Subject to this disclaimer,

WHAT WE CLAIM IS:-

1. A curable coating composition which comprises a mixture of

A) one or more olefinically unsaturated compounds having a molecular weight of from 70 to 20,000 and a boiling point at standard pressure of above 50°C and

B) one or more vinylurethanes copolymerizable with A) but differing therefrom,

in which mixture component (B) is a reaction product of vinyl isocyanate and a polyol having a molecular weight of less than 500 and the weight ratio of the components A:B is from 99:1 to 30:70.

2. A composition as claimed in claim 1, in which the component (A) has a vapor pressure of less than 10 mm Hg at 100°C.

3. A composition as claimed in claim 1 or 2, in which component (A) is at least one material selected from esters of unsaturated monocarboxylic acids or dicarboxylic acids with aliphatic, cycloaliphatic or aromatic-aliphatic monohydric to tetrahydric alcohols of 3 to 20 carbon atoms, amides of acrylic acid or methacrylic acid which may or may not be substituted by alkyl, alkoxy-alkyl or hydroxyalkyl at the nitrogen, unsaturated polyesters having a molecular weight of from 500 to 5,000 and containing from 0.5 to 10 double bonds per 1,000 molecular weight units, unsaturated epoxy resins, unsaturated polyurethanes obtained from hydroxyalkyl acrylates and diisocyanates with or without polyols or polyamines, reaction products of copolymers containing maleic anhydride groups with unsaturated alcohols, and reaction products of acrylic ester copolymers or polyesters containing carboxylic acid groups with olefinically unsaturated epoxides.

4. A composition as claimed in any of claims 1 to 3, in which the polyol used to manufacture the component (B) has a molecular weight of less than 400.

5. A composition as claimed in any of claims 1 to 4, in which the weight ratio of components A:B is from 95:5 to 50:50.

6. A composition as claimed in claim 1 and substantially as described in any one of the foregoing Examples.

7. A composition as claimed in any preceding claim when coated on a surface and cured by irradiation by means of an electron beam.

8. A printing ink or printing paste, or a photopolymer layer for a print carrier, containing a curable composition as claimed in any one of claims 1 to 6.

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